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European Patent Office  
Office européen des brevets

Publication number

0 032 443  
A2



## EUROPEAN PATENT APPLICATION

(3) Application number 81300095.7

(72) Inventor B 29 D 11 00

(3) Date of filing 09.01.81

C 08 F 246/00, G 02 C 7/04

(50) Priority: 10.01.80 GB 8000809

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(43) Date of publication of application:  
22.07.81 Bulletin 81/29

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(64) Designated Contracting States:  
AT BE CH DE FR GB IT LI NL SE

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(54) Cross-linked polymers for contact lenses.

(57) Contact lenses are disclosed which are formed from hydrophilic polymers of at least one hydrophilic monomer and minor proportions of at least one monomer containing cationic groups and at least one monomer containing anionic groups so that ionic cross-linkages can form between polymer molecules. Typical monomers containing cationic groups are alkyl amino acrylates and methacrylates and typical monomers containing anionic groups are methacrylic and acrylic acids and such monomers may be employed in proportions by weight of from about 5% to about 20%. Suitable hydrophilic monomers include hydroxy alkyl acrylates and methacrylates.

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CROSS-LINKED POLYMERS FOR CONTACT LENSES

The present invention relates to hydrophilic polymers having ionic cross-linkages, contact lenses formed therefrom and a process for their preparation.

5    BACKGROUND OF THE INVENTION

Cross-linking of polymers is well-known in the art for providing polymers with desirable properties, in particular desirable mechanical properties such as high tensile strength. Cross-linking is usually effected by 10 use of a covalent cross-linking agent which bridges two or more polymer chains linking them together by covalent bonding. Cross-linking can also be effected by means of electrovalent interactions involving ionized sites in neighbouring polymer chains; cross-links induced in this 15 way are known as ionic cross-links. This form of cross-linking is illustrated by ionomer resins which are ethylene copolymers containing pendant carboxylic acid groups and an associated bivalent metal cation and also by polyelectrolyte complexes which consist of an essentially neutralized 20 mixture of polycations (e.g. a polyquaternary ammonium compound and a polyanion such as poly(vinyl sulfonic acid)).

Cross-linking of hydrophilic polymers for use as contact lens materials is often a practical necessity in 25 order that the material has adequate mechanical properties in the hydrated state. Covalent cross-linkage has been widely used for this purpose but ionic cross-linking has not hitherto been used. Ionic cross-linking requiring the

presence of a bivalent metal cation is not acceptable for contact lens material since in use the bivalent cations are largely leached from the polymer by tear fluid and replaced by sodium and potassium ions contained in the tear 5 fluid; polyelectrolyte complexes are unsuitable since they cannot conveniently be prepared in a form suitable for machining on a lathe.

BRIEF DESCRIPTION OF THE INVENTION

According to one aspect of the invention, there 10 is provided a novel polymer for use as a contact lens material and comprised of chains in each of which there are both cationic and anionic sites participating in electrovalent cross-linkage of the chains one to another, the aforesaid sites being provided by moieties of the polymer 15 chains which are resistant to loss of polarity by contact with tear fluids.

In a more specific embodiment the invention provides a contact lens which comprises a hydrophilic polymer of at least one hydrophilic vinyl or vinylidene 20 monomer, a minor proportion of a cationic group - containing monomer and a minor proportion of an anionic group - containing monomer and said ionic group - containing monomers providing cationic and anionic sites for ionic cross-linkages between polymer chains.

25 The moieties providing the ionic sites will usually be organic moieties polymerized into the polymer chains and, in general such organic moieties will be units

of monomer material copolymerized into a backbone polymer. The monomer material may, for example, be an alkyl aminoacrylate or methacrylate, such as dimethylaminoethylmethacrylate, t-butylaminoethylmethacrylate or di-n-butylaminoethylmethacrylate, in the case of monomer material providing cationic sites. Conveniently methacrylic or acrylic acid may be employed to provide anionic sites although other polymerizable carboxylic acids may be used. Alternatively, however, such other cationic and anionic moieties as quaternary ammonium compounds and unsaturated sulfonic acids may be employed to provide the cationic and anionic sites although, it should be noted, particularly in the case of relatively strongly ionizing groups, that there may be difficulties as regards availability of materials. Vinyl sulfonic acid, styrene sulfonic acid and unsaturated phosphoric acid monomers are however, obtainable.

The polymers of the invention will normally contain the ionic moieties in a comparatively minor proportion together with a balance of polymerized essentially non-ionic monomer material. The balance may, for example, be made up of polymerized hydrophilic monomer such as an hydroxy alkyl acrylate or methacrylate, e.g. 2-hydroxyethylmethacrylate or N-vinylpyrrolidone and/or a polymerized hydrophobic monomer, such as an alkyl acrylate or methacrylate or styrene or a substituted styrene. Typical hydrophobic monomers are methyl methacrylate and n-butyl methacrylate.

Copolymers of 2-hydroxyethylmethacrylate with dimethylaminoethylmethacrylate, methacrylic acid and optionally styrene have been found to be especially suitable for use as soft contact lens material.

5       The anionic moieties may be present in substantially stoichiometrically equivalent amounts, but, if desired, one ionic moiety may be in stoichiometric excess. For example, a stoichiometric excess of the anionic moiety provides a powerful hydration mechanism in the alkaline  
10      environment of the eye so that in most instances such an excess will be considered desirable. In such cases, where the ionic groups are in excess they are preferably neutralised by treatment of the final polymer with a mildly alkaline solution as described in British Patent No. 1,548,158  
15      (the disclosure of which is specifically incorporated herein by reference).

As indicated earlier, the ionic moieties will in general be present in relatively minor proportions. Generally the proportion of ionic moieties available for  
20      participation in electrovalent linkage will be in the range from about 5% to about 20% by weight, preferably 7% to 20% (e.g. from about 7% to 17% by weight). In all cases, the percentages stated are by weight of the whole unhydrated polymer.

25       Polymers according to the invention can conveniently be made by polymerizing a monomer mixture comprising components of identity and content appropriate to the desired polymer, the polymerization being effected using, for example, azobisisobutyronitrile as initiator. Other

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initiators may alternatively be employed although peroxide initiators are not at present recommended since they have been found to produce dark coloured polymers.

The polymers of the invention have been found, 5 as will be appreciated from the Examples which follow, to exhibit good mechanical properties. This is thought to be a result of the labile character of the electrovalent cross-linkage forces which results in the polymeric material being able to yield locally to applied stress. The polymers of the invention may, in addition to cross-linkages as a result of electrovalency, contain covalent cross-linkages as a result of use, if desired, of a covalent cross-linking agent, and results in polymers having even better mechanical properties. Covalent cross-linkages may be incorporated in 15 the polymers by including a di- or poly functional cross-linking agent, such as glycol dimethacrylates or acrylates, allyl methacrylate or acrylate or triallyl cyanurate.

The polymer of the invention can readily be cast to form a lens or lens blank. Lens blanks can be machined 20 in known manner to form contact lenses of desired configuration. Lenses made in this way from hydrophilic monomer-derived polymers can be hydrated to equilibrium after machining using saline solution as described, for example, in British Patent No. 1,548,158.

25 The invention includes within its scope lenses, blanks and machined lenses as just described and in particular includes such lenses and lens blanks made of polymer

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comprising the following polymerized monomer units in the following proportions by weight:-

2-hydroxyethylmethacrylate: 24 parts  
(2-HEMA)  
5 dimethylaminoethylmethacrylate: from 1 to 2.25 parts  
(DMAEMA)  
methacrylic acid: from 1 to 3 parts  
(MA)  
styrene: up to 2.5 parts

10 The following specific Examples are intended to illustrate the invention.

Examples 1 to 5

Polymers were prepared according to the formulations given in Table 1. 2-hydroxyethylmethacrylate (2-HEMA) with a very low (0.05 wt%) ethylene glycol dimethacrylate (EGDM) content was used and hence the polymer was expected to contain a very low concentration of derived covalent cross-links. The monomer mixtures were polymerized by thoroughly mixing together purified 2-HEMA, redistilled MA, DMAEMA and (where stated styrene) in the proportions stated in Table 1 using the stated quantity of azodiisobutyronitrile (AZDN) as free radical generator. Polymerization was carried out in polythene tubes at 65°C for 16 hours, followed by curing 20 for 3 hours at 100°C. In the case of comparison Examples 1 and 3, the DMAEMA was omitted, as indicated.

The rods obtained were cut into lens blanks, machined to form lenses, extracted and hydrated to equilibrium in a saline solution buffered at pH7.4. The

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properties were then determined and the results are presented in Table 2. It can be seen that polymers of high tensile strength, as judged by the burst test, can be prepared even in the apparent absence of covalent cross-links.

This observation and the fact that the water content of the gels containing DMAEMA are somewhat lower than those without, in spite of the hydrophilic nature of DMAEMA and twice the addition of methacrylic acid, provides convincing evidence that hydrogels which contain minor proportions of cationic and anionic sites contain physically-effective cross-links attributable to the simultaneous presence of both types of ionic site.

TABLE 1.

15

	1	2	3	4	5
2-HEMA (purified) (g)	24.00	24.00	24.00	24.00	24.00
DMAEMA (g)	0.00	1.23	0.00	2.00	2.00
Methacrylic Acid (g)	0.68	1.20*	1.77	2.09*	2.66
Styrene (g)	0.00	0.00	2.05	2.05	2.05
AZDN (g)	0.02	0.02	0.03	0.03	0.03

\* stoichiometric excess with respect to the amount of dimethylaminoethylmethacrylate (DMAEMA)

20  
25

TABLE 2

	Example No.	Extractable Content (% w/w)	Water Content (% w/w)	Swell (%)	Burst Pressure/Lens Thickness
5	1 (comparison)	6.3	64	46	8 psi/0.21mm
	2	7.9	59	35	16 psi/0.20mm
10	3 (comparison)	5.5	71	55	8 psi/0.20mm
	4	11.5	55	32	19 psi/0.20mm
	5	8.8	64	42	15 psi/0.21mm

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CLAIMS

1. A polymeric contact lens formed by addition polymerization of at least one hydrophilic, ethylenically-unsaturated monomer, an ethylenically-unsaturated monomer containing a cationic group and an ethylenically-  
5 unsaturated monomer containing an anionic group, said cationic and anionic groups forming ionic cross-linkages whereby the lens exhibits improved burst strength as compared with a similar lens containing no ionic cross-linkages.
- 10 2. A contact lens according to claim 1 wherein the monomer containing a cationic group is a vinyl or vinylidene monomer having an amino group or quaternary ammonium group.
- 15 3. A contact lens according to claim 2 wherein the vinyl or vinylidene monomer is an alkyl amino acrylate or methacrylate.
- 20 4. A contact lens according to any one of the preceding claims wherein the monomer containing an anionic group is a vinyl or vinylidene monomer having a carboxylic or sulfonic acid group.
- 25 5. A contact lens which comprises a polymer of a hydrophilic vinyl or vinylidene monomer containing a single center of unsaturation, a cationic vinyl or vinylidene monomer having alkyl amino or quaternary

ammonium cationic groups and an anionic vinyl or vinylidene monomer having carboxylic or sulfonic acid anionic groups, said cationic and anionic groups constituting pendant or terminal groups in the polymer which interact to form ionic cross-linkages.

5 6. A contact lens according to claim 5 wherein the anionic monomer is present in the polymer in stoichiometric excess with respect to the cationic monomer.

7. A contact lens according to claim 5 or claim 6 wherein the cationic and anionic monomers are present 10 in the polymer in a total amount of from about 5 to about 20% by weight..

8. A contact lens according to any one of claims 5 to 7 wherein the polymer also contains covalent cross-linkages derived from cross-linking monomers containing 15 at least two centers of unsaturation.

9. A contact lens according to any one of claims 5 to 8 wherein the polymer is an addition polymer of at least one hydrophilic monomer and at least one hydrophobic monomer.

20 10. A contact lens which comprises a polymeric hydrogel which is the hydrated polymerized product of a monomer mixture comprising a minor proportion by weight of vinyl or vinylidene monomers containing cationic and anionic groups and a major proportion of polymerizable 25 monomer having a single center of unsaturation, said monomer mixture including sufficient hydrophilic monomer to render the resultant polymer hydrophilic and the



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European Patent Office  
Office européen des brevets

Publication number:

0 032 443

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## EUROPEAN PATENT APPLICATION

Application number: 81300095.7

Int. Cl. B 29 D 11/00

Date of filing: 09.01.81

C 08 F 246/00, G 02 C 7/04

(30) Priority: 10.01.80 GB 8000809	(72) Inventor: Atkinson, Ivor B. 32 Mount Road Chessington Surrey(GB)
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(38) Date of deferred publication of search report: 14.10.81	(72) Inventor: Holdstock, Barry C. 67 Northway Morden Surrey(GB)
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monomers containing cationic and anionic groups being effective in forming ionic cross-linkages in the resultant polymer.

11. A hydrophilic polymer which comprises an addition polymer of at least one hydrophilic vinyl or vinylidene monomer, a minor proportion by weight of a copolymerizable monomer containing anionic groups and a minor proportion by weight of a copolymerizable monomer containing cationic groups, the anionic and cationic groups forming ionic cross-linkages.
12. A method of preparing a hydrophilic copolymer containing ionic cross-linkages which comprises subjecting to polymerization in the presence of a free-radical initiator a monomer mixture comprising at least one hydrophilic vinyl or vinylidene monomer containing a single center of unsaturation, a vinyl or vinylidene monomer containing a cationic group and a vinyl or vinylidene monomer containing anionic groups.



European Patent  
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EUROPEAN SEARCH REPORT

0032443

Application number

EP 81 30 0095

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>US - A - 4 172 177</u> (B. SATO)		B 29 C 11/00
A	<u>US - A - 4 071 650</u> (J.R. CROSS)		C 08 F 246/00
A	<u>US - A - 4 041 020</u> (J.R. CROSS)		C 02 C 7/04
A	<u>US - A - 3 926 756</u> (A.J. RESTAINO)		
A	<u>US - A - 3 634 366</u> (K. CHUJO et al.)		
PA	<u>US - A - 4 218 554</u> (W. FOLEY)		
PA	<u>US - A - 4 212 782</u> (M. KLEIN)		
DA	<u>GB - A - 1 548 158</u> (GLOBAL VISION)	-----	
			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			B 29 D 11/00 G 02 C 7/04 C 08 F 212/14 220/04 220/06 220/34 228/00 228/02
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			& member of the same patent family, corresponding document
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	23-07-1981	VAN THIELEN	